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INCREASE IN CAST DENSITY IN PRODUCTION OF SILICON NITRIDE ARTICLES OF IRREGULAR SHAPE

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The effect of modifying organic additives on the tenacity of ethyl silicate binders and the strength of castings based on Si_3N_4 ultradisperse powder is studied. The effect of the modified Si_3N_4 powder together with the combined sol-gel composition on the density and strength of the castings is demonstrated.

Production of structural ceramic articles of irregular shape is associated with substantial difficulties. The most common technology for this production is aqueous and thermoplastic slip casting [1 – 3]. Aqueous solutions of PVS are generally used as the liquid phase in slip casting of Si_3N_4 powders. The density of the unfired slip casting intermediate product is 1870 kg/m^3 which is 20% more than that of the articles of crude Si_3N_4 produced by hydrostatic molding. The apparent density of the fired material is 3220 kg/m^3 , and its ultimate strength reaches 974 MPa (USA patent 4624812). The silicon nitride articles produced by slip casting have insufficient heat resistance and great firing shrinkage.

The use of thermoplastic slips ensures the mechanical strength and stability of the product's properties, including high accuracy of the product dimensions due to the absence of shrinkage. In the large-scale production of articles of irregular shape from Si_3N_4 -based materials, the injection molding method (USA patent 4708832) is used which allows a product density equal to 95% of the theoretical density. The injection-molded materials have a homogeneous fine-grained structure, the apparent density of $2000 - 2700 \text{ kg/m}^3$, and high strength parameters (Weibull modulus of no less than 20).

The silicon nitride ceramic is not very susceptible to sintering due to its rigid covalent bonds and low atomic mobility. To intensify sintering, such additives as MgO , Y_2O_3 , Al_2O_3 and others are used at the rate of 5 – 10% (henceforward mass content is indicated) providing for formation of a liquid phase that facilitates compaction of the material [4].

The use of sols in molding of irregularly shaped products helps to eliminate numerous packing defects which reduce the strength of the material [5]. The application of sol-gel compositions filled with carbon makes it possible to synthesize silicon nitride crystals at a temperature of 1400°C . Note that in order to implement complete synthesis, the ratio $\text{SiO}_2 : \text{C}$ should be 1 : 2.

Lately the use of sol-gel compositions in production of articles of irregular shape is attracting great attention since these compositions make it possible to modify the phase composition and structure of the materials, develop different compositions containing $\beta\text{-SiC}$ and $\alpha\text{-Si}_3\text{N}_4$ which are synthesized at temperatures much below the usual ones (Japan patent application 61-183370). The use of high pressures in hydrostatic treatment of castings in order to improve ceramic properties is considered promising.

The purpose of the present work is to study the effect of different technological parameters on compaction of castings made of self-hardening mixtures based on finely ground Si_3N_4 powder and ethyl silicate binders. The authors studied the physicomaterial properties of the material based on Si_3N_4 and sol-gel self-hardening binder made of ethyl silicate hydrolyzed without organic solvents and an organic plasticizer. Yttrium and aluminum oxides were used as sintering additives. Lignin sulfonate (LST), polyvinyl acetate (PVAD), and triethanolamine (TEA) which can be introduced into the mixture in the course of ethyl silicate hydrolysis were used as plasticizers.

The initial Si_3N_4 powder was represented by the aggregates of irregular shape consisting of isometrically shaped grains and needle-like crystals of Si_3N_4 .

The Si_3N_4 powders and sintering additives were crushed to particles with a prevalent size below $1 \mu\text{m}$. Grinding was carried out in a ball mill and planetary mill. In the course of grinding, the Si_3N_4 powders were modified with an elemental organic compound, i.e. silicon alkoxide. The effect of the amount of silicon alkoxide on the grinding efficiency and powder parameters were investigated (Fig. 1 and 2)

It was found that after 4 – 6 h grinding in the ball mill the aggregates of Si_3N_4 10 – 15 μm in size prevailed. After grinding for 32 h, the grains of Si_3N_4 were represented by fragments of prismatic and needle-shaped crystals. It is essential to note that in grinding in the ball mill, the prevalent

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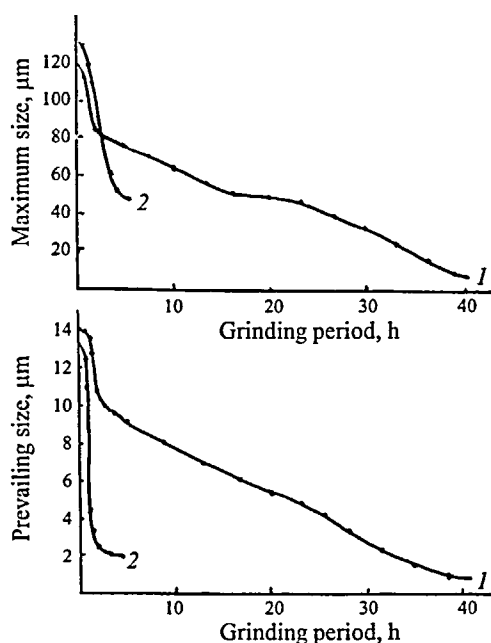


Fig. 1. Variation of the size of Si_3N_4 particles depending on the type of mill: 1 and 2) ball mill and planetary mill, respectively.

size of Si_3N_4 grains was $1\text{ }\mu\text{m}$ and at the same time certain particles of a maximum size of nearly $10\text{ }\mu\text{m}$ were found, and the powder crushed in the Sand planetary mill exhibited many more particles of the maximum size (up to $40\text{ }\mu\text{m}$) while the prevailing size was below $2\text{ }\mu\text{m}$. Therefore in production of experimental samples, silicon nitride was ground in ball mills with the addition of an organoelemental substance which intensifies the grinding process (Fig. 2) with simultaneous modification which affected the subsequent physicochemical processes in the course of hardening and sintering of the mixtures [7].

In order to increase the plasticity and tenacity of the self-hardening binder and decrease hardening shrinkage, LST, PVAD, or TEA additives were introduced in the ethyl silicate hydrolyzate. The hardening kinetics of the binders were investigated by the variation in the relative electric conduction of sols. The electric conduction was measured with a R-383 digital voltmeter. A closed cell with a distance of 27 mm between electrodes was used. The electrodes were made of IX18N9T stainless steel.

To increase the strength of the castings, it is more convenient to use ethyl silicate binders containing polyethoxysilanes, whose polycondensation produces stronger $\text{Si}-\text{O}-\text{Si}$ bonds than polysilicic acids. However, the powders of finely ground silicon nitride, as well as sand have a great specific surface area, which requires the introduction of substantial quantities of binder. Since a high content of SiO_2 can impair the high-temperature properties, the products of hydrolysis of ethyl silicate were used as the binders. The amount of water used in preparation of ethyl silicates was selected to obtain polysilicic acids.

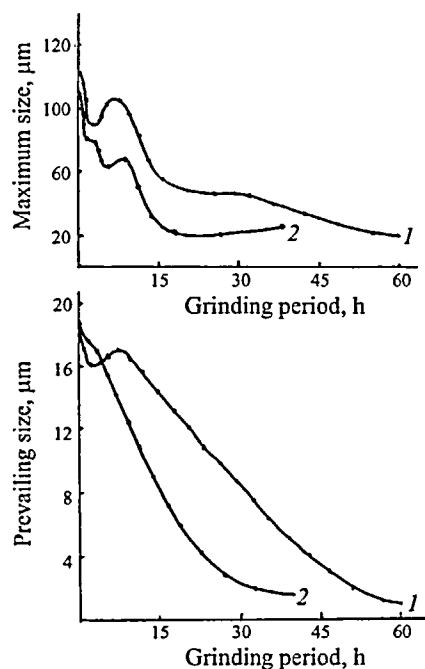
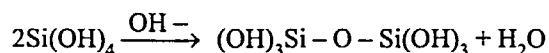


Fig. 2. Variation of the size of Si_3N_4 particles depending on the duration of grinding in the ball mill with addition of 0.1% (1) and 0.6% (2) organoelemental substance.

Figure 3 shows the electric conduction of modified sol-gel binders based on ethyl silicate hydrolyzed with a great amount of water without organic solvents (ETS 32/60). The sols are based on polysilicic acids since the amount of water used in hydrolysis was above the stoichiometric value [8]. The application of the acid additives accelerates the rate of the hydrolysis reaction. In weakly acid medium, the hydrolysis rate falls behind the rate of molecular condensation. Hydrolyzed solutions possessing the maximum stability in ethyl silicate the given concentration of SiO_2 have their pH within the limit of 1.5 to 3.

The reaction between polysilicic acids and LST results in a decrease in the electric conduction. However, when substantial (up to 5%) quantities of LST are added, the electric conduction rises sharply, which is related to the increased mobility of the binder due to a decrease in the rate of polycondensation of the product of ethyl silicate hydrolysis (Fig. 3).

The introduction of TEA changes the acid pH of the medium to the basic pH, thus accelerating sol-gel conversion. With an increase in the TEA quantity from 0.5 to 1.5%, sharp acceleration of gel formation was observed accompanied by a decrease in electric conduction. The alcohol released raises the electric conduction, and the water produced by self-condensation of polysilicic acid as the result of the reaction



facilitates secondary hydrolysis which, in turn, decreases anew the electric conduction.

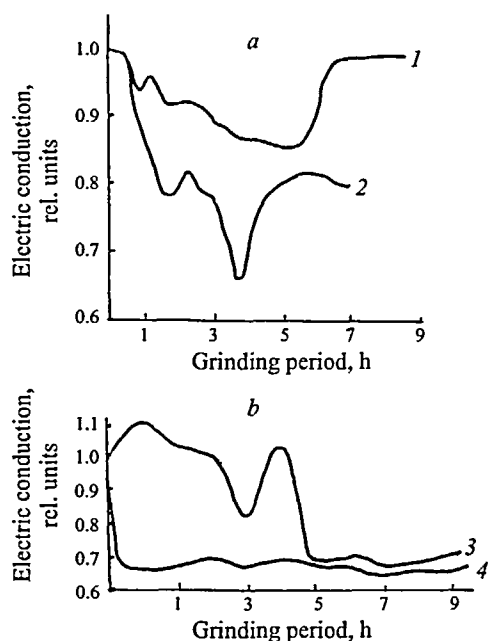


Fig. 3. Hardening kinetics of sol-gel compositions (ETS 32/60) with addition of LST (a) and TEA (b). 1) ETS 32/60; 2) 2% LTS; 3) 0.5% TEA; 4) 1.5% TEA.

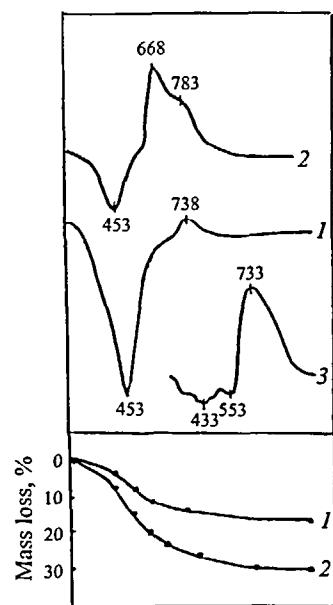


Fig. 4. DTA curves and mass loss of ethyl silicate gel (1), gel consisting of a mixture of ethyl silicate and TEA (2), and TEA (3).

The introduction of large quantities of TEA in sol-gel compositions is undesirable, since it significantly lowers the tenacity of the binders. Heat treatment of gel with TEA additive reveals significant mass loss (Fig. 4). This may be evidence of the fact that introduction of TEA in sol delays polymerization of the polysilicic acid resulting from hydrolysis of ethyl silicate, and in addition, the water released in polycondensation is captured by the gel cluster.

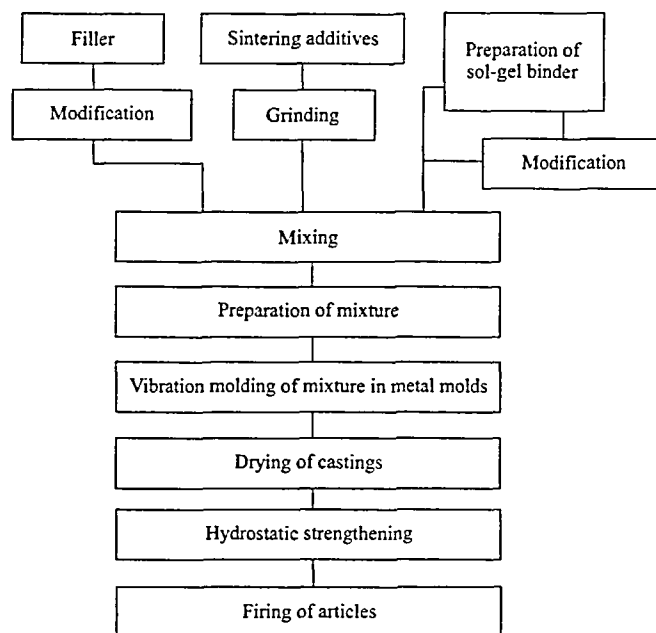


Fig. 5. Technological procedure for the production of articles of irregular shape.

The shape and slope of the curve of differential thermal analysis (DTA) change on introduction of the TEA additive. The rate of removal of adsorbed moisture (OH-groups) from the gel surface increases within the temperature intervals of 293 – 389 and 389 – 628 K. The exothermic effect of oxidation of the products of thermal degradation of TEA is superimposed on the exothermic effect of removal of the hydroxyl groups located inside the alumina frame, which results in modification of the shape of the DTA curve.

The exothermic effect in the temperature interval of 653 – 853 with its maximum at 738 K on the gel DTA curves reflects the destruction of the OC_2H_5 ethoxy groups related to the silicon-oxygen frame which remain in the xerogel. The destruction of these groups is also accompanied by weight loss and coincides in its rate with removal of the hydroxy groups located inside the alumina frame. Therefore, it can be contended that the processes of removal of H_2O clathrates and destruction of ethoxy groups proceed at the same rate. It can be attributed to the fact that the latter are also located inside the alumina frame in the form of clathrates.

Upon introduction of TEA, the rate of removal of both OH groups and OC_2H_5 groups increases, but the rates are different. The OH-groups are removed more intensively than in the usual gel, since owing to polycondensation of polysilicic acid and polymerization of hydrolysis products with a small quantity of water, various structures emerge which largely differ in the strength of their bonds. The mass loss for the gel with TEA additive is nearly twice the mass loss for gel with HCl hydrolysis catalyst (Fig. 4) with a low rate of temperature elevation in the course of heating.

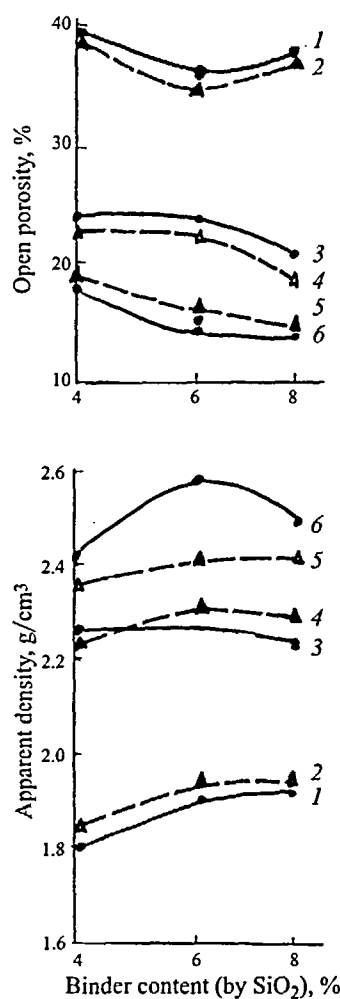


Fig. 6. Dependence of apparent density and open porosity of the castings on the hydrostatic treatment pressure and the amount of modifying additive. Silicon alkoxide content: 1, 3, 6) 0.1%; 2, 4, 5) 0.6%. Hydrostatic treatment pressure: 1, 2) 0; 3, 4) 1 MPa; 5, 6) 2 MPa.

At high heating rates, the reaction between the organic plasticizers and polysilicon acids, which are the polymerization products resulting from hydrolysis of ethyl silicates with large quantities of water, should lead to the emergence of Si-O-C bonds, and this stimulates the appearance of a Si-C bond in thermal degradation in the case of a shortage of oxygen and can result in the formation of SiC on firing of the gels.

The binders based on hydrolyzed ethyl silicate with and without LST and TEA additives were tested for production of articles of irregular shape.

The technological procedure for production of articles of irregular shape based on silicon nitride and ethyl silicate binders is shown in Fig. 5.

The effect of LST and TEA additives in ethyl silicate binder containing different quantities of water under hydro-

lysis on compaction of the samples under hydrostatic compression was studied as well. It was found that the apparent density of the material increases with an increase in the quantity of ethyl silicate in the hydrolyzate regardless of the pressure of the hydrostatic treatment, and the shrinkage grows with an increase in the pressure. On introduction of the plasticizing additives specified, the application of hydrostatic treatment does not lead to compaction of the vibration-molded mixture material based on ethyl silicate binders. This encouraged the search for a more efficient plasticizer to be used in the composition of self-hardening mixtures based on ethyl silicate binders for the production of articles of irregular shape based on Si₃N₄.

The use of modified Si₃N₄ powder in the composition of the mixtures based on ethyl silicate binders increases the density of the cast samples after their hydrostatic compression, and an increase in the apparent density accompanied the increase in pressure and the quantity of ethyl silicate (by SiO₂) in the binder. The results of the experiments showed that with an increase in the quantity of the silicon alkoxide modifying additive and the pressure of the hydrostatic treatment, the apparent density of the casting grows and the open porosity decreases by more than half (Fig. 6).

Thus, use of the modified Si₃N₄ powder provides for greater compaction of castings based on silicon nitride and ethyl silicate binder.

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